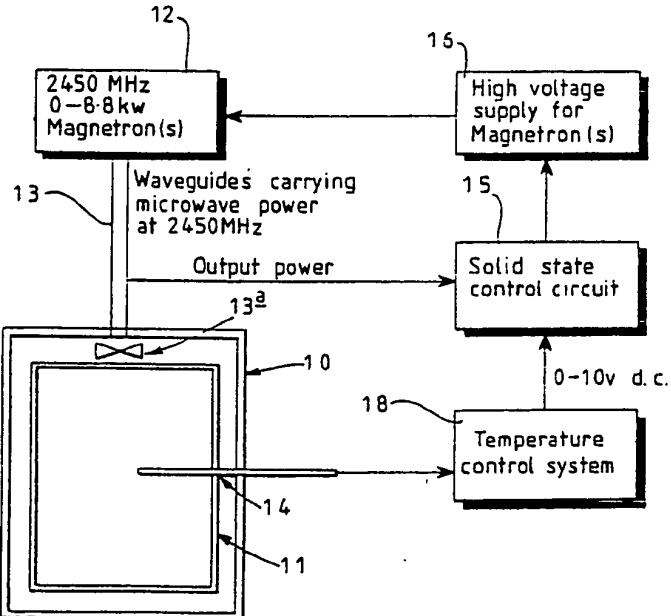




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :	A1	(11) International Publication Number: WO 93/12629 (43) International Publication Date: 24 June 1993 (24.06.93)
H05B 6/80		
(21) International Application Number: PCT/GB92/02277		(81) Designated States: AU, CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 9 December 1992 (09.12.92)		
(30) Priority data: 9126560.3 13 December 1991 (13.12.91) GB		Published With international search report.
(71) Applicant (for all designated States except US): STAFFORD-SHIRE UNIVERSITY ENTERPRISES LIMITED [GB/GB]; Beaconside, Stafford ST18 0AD (GB).		
(72) Inventors; and		
(75) Inventors/Applicants (for US only) : BOWDEN, Alan, Leslie [GB/GB]; 25 Knowle Road, Weeping Cross, Stafford ST17 0DN (GB). HAMLYN, Michael, Gower [GB/GB]; 1 Austin Friars, Stafford ST17 4AP (GB).		
(74) Agents: MOSEY, Stephen, George et al.; Marks & Clerk, Alpha Tower, Suffolk Street Queensway, Birmingham B1 1TT (GB).		

## (54) Title: MICROWAVE HEATING METHOD AND APPARATUS



## (57) Abstract

Apparatus for heating items (19) of ceramic material by microwave energy comprises a microwave resonant cavity (10), a refractory box (11) within the cavity to receive the items (19), a magnetron (12) for generating microwaves, a thermal screen (24) around the items (19), in use, to be heated by the energy of the microwaves, and means (15-18) for continuously controlling the power of the magnetron (12) in response to any difference between a set value of the temperature of the items and a measured value thereof. Heated gas can be passed through the screen and around the items during the microwave heating process, and the susceptibility of the thermal screen to heating is determined by doping or spray coating with susceptors. In one embodiment the thermal screen can also be electrically heated.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Bahamas	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	CR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Thailand
CZ	Czech Republic	MC	Mongaco	TG	Togo
DE	Germany	MD	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

MICROWAVE HEATING METHOD AND APPARATUS

This invention relates to a microwave heating method and apparatus, particularly for sintering/firing ceramic materials such as pottery, industrial ceramics and the like, in large batches of an industrial scale.

Ceramic materials generally absorb little electromagnetic energy at microwave frequencies at room temperature. However at higher temperatures their ability to absorb microwave energy can increase considerably, as shown in Figure 1 which is a graph of power absorbed against temperature. This can cause rapid, localised heating in a ceramic piece, should the temperature within the piece be, or become, non-uniform. This is particularly true at temperatures above temperature 'A' in Figure 1. The phenomenon is known as 'thermal runaway'.

In addition to preventing 'thermal runaway' efficient and effective heating of a piece also requires uniformity of temperature at any time throughout a piece. Two causes of temperature non-uniformity are firstly attenuation of the electric field, and hence power generated, with depth into the piece, and secondly radiation of heat energy from the surface of the heated body.

The degree of attenuation of power within a piece increases with power dissipation within the piece, to which it is mathematically related. Since power dissipation can increase significantly with temperature (Figure 1) the depth within the piece in which significant power is generated (known as the depth of penetration) can decrease significantly. Should the depth of penetration decrease such that it becomes comparable with the dimensions of the piece then the processing time must be extended to allow equalisation of

temperature throughout the piece by thermal conduction. A final, stable situation is reached when the power input becomes constant for a set temperature. In practice, the depth of penetration is normally much greater than the dimensions of ceramic pieces and thus the attenuation of the electric field is not a problem.

However radiation of heat energy is a more serious problem. Although thermal insulation can be used to prevent loss of heat energy, the ambient temperature in the applicator containing the pieces to be fired will still be significantly less than that of the surface of a piece. Hence radiation of energy from the surface causes a thermal gradient to be created between the surface and the body of a piece, as shown in Figure 3. This problem is the most significant one to be overcome in manufacturing a commercially acceptable ceramic product on an industrial scale.

The object of the present invention is to overcome or at least mitigate all or some of the problems referred to.

According to one aspect of the invention there is provided a method of heating ceramic material in an interior of an enclosure, comprising providing a variable power source of microwave energy, providing in said interior of the enclosure a thermal screen which is around the ceramic material, in use, and which is heated by said microwave energy, operating said source to supply microwave energy to said interior of said enclosure containing said ceramic material, in use, and continuously controlling the power of said source in response to a difference between a set value of a parameter of the system, and a measured or calculated value of the parameter during operation of the method.

Preferably the method includes passing heated gas/air into the interior of the enclosure and around the ceramic material. Desirably the hot gas/air is circulated in a closed system containing a fan.

According to another aspect of the invention there is provided apparatus for heating ceramic material comprising an enclosure having an interior in which said ceramic material is intended to be received, a thermal screen in said interior around said ceramic material, in use, a variable power source of microwave energy outside the enclosure operable to supply microwave energy to said interior of the enclosure containing said ceramic material, in use, and means for continuously controlling the power of said source, in use, in response to a difference between a set value of a parameter of the system, and a measured or calculated value of the parameter during the heating.

The invention will now be described, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a graph showing a known relationship between absorption of microwave power and temperature for ceramic materials,

Figure 2 is a block diagram of part of a system of the present invention for providing accurate control of temperature sufficient to prevent thermal runaway whilst heating ceramic materials by microwave energy,

Figure 3 is a graph showing the relationship between temperature and the depth of a ceramic article when the article is heated by a known microwave heating method,

Figure 4 diagrammatically shows the stacking of ceramic articles to be heated by a method of the invention,

Figure 5 diagrammatically shows the passing of heated gas through an enclosure according to the present invention,

Figure 6 is a diagram showing the use of a thermal screen with the method of the present invention, and

Figure 7 is a block diagram of the method of the present invention.

As explained, the phenomenon known as 'thermal runaway' can be a problem with the heating of ceramic materials by microwave energy. To prevent this problem, it is necessary to detect rapid increases of temperature or rate of energy absorption of the ceramic piece and correspondingly to reduce the rate of microwave energy input, or power, into the piece. Therefore continuous control of the microwave energy source is necessary to achieve uniform heating of the piece.

The arrangement shown in Figure 2 is an arrangement for preventing thermal runaway.

Shown in Figure 2 is a basic system for sintering ceramic materials. The values of frequency, power and volts shown are by way of example only. The system has a microwave resonant cavity 10 within which is contained a refractory box 11 for containing therein the ceramic article or articles to be sintered. A source of microwave energy, such as a magnetron 12, is coupled to the cavity 10 directly, or indirectly such as by a waveguide 13. One or more optical fibre probes 14 are inserted directly into the refractory box and placed near

to or in contact with the surfaces of the piece or pieces whose temperature is to be measured. The optical probes represent only one possible means of temperature measurement.

The desired control of the microwave energy source is achieved by an electronic circuit containing one or more solid state devices, and indicated at 15, the solid state device being, for example, a thyristor with its control circuit, the thyristor controlling the voltage supply indicated at 16, to the magnetron. The control signal to the thyristor may be derived, as shown in Figure 2, from either the temperature of the piece or alternatively from the power output of the magnetron. It can be a directly measured value of the chosen parameter or could be calculated from the measured value of a different parameter.

The control signal is compared with a set temperature or power value and a difference or error signal, if present, is fed to the thyristor control. Since energy radiated by the magnetron generator is converted directly to heat energy within the ceramic piece, a change in energy generated by the magnetron causes an instantaneous change in energy absorbed by the piece. The set temperature may be programmed by computer to follow a pre-set temperature-time profile or a power-time profile to obtain the required characteristic of the piece or pieces in the minimum time.

Figure 2 shows a temperature control system 18, which can incorporate a suitable computer. The temperature of a piece is sensed by the optical fibre thermometry system. Thermocouples are not suitable since they cannot be placed permanently within the cavity 10 or refractory box 11 because they are metallic. Infra-red pyrometry can be used by viewing the piece from outside

the cavity 10 through a port in the walls of the cavity and refractory box respectively. As mentioned, power from the magnetron source is, in one example, fed into the cavity 10 through the waveguide 13. The cavity is preferably multimodal, namely it will support a large number of resonant modes in a given frequency range, and in a preferred embodiment the cavity can have a mode stirrer 13a to provide greater uniformity of electric field distribution within the cavity. To heat large quantities, or a batch, of ceramic pieces, an array of magnetrons may be required. Thus by varying the voltage supply to the magnetron, the magnetron effectively provides a variable power source of microwave energy, so that the temperature of the piece can be controlled to prevent thermal runaway.

As mentioned, whilst the system shown in Figure 2 can provide accurate control of temperature sufficient to prevent such thermal runaway, it cannot provide uniformity of temperature at any time throughout a piece due to the electric field attenuation and heat energy radiation previously referred to. As explained, the attenuation of the electric field is not, in practice, a problem. The present invention does however relate to the problem of preventing loss of heat energy by radiation and the ways in which this problem can be tackled are shown in Figures 4 to 6. These figures show techniques for overcoming or at least mitigating this problem for batch production of ceramic products of varying dimensions, geometry and process temperatures.

Figure 4 shows one possible scheme for stacking individual ceramic items 19 in the refractory box 11. This is just one form of stacking where the pieces are so arranged that temperature gradients between the centre and edges of the pieces due to conduction and radiation are minimised.

Turning now to Figure 5, another technique for reducing or preventing loss of heat energy is to pass hot air or other gas or gases through the refractory box 11 and around the ceramic pieces to assist the equalisation of temperature throughout the refractory box. This is particularly advantageous in establishing a uniform temperature up to temperature A in Figure 1. It is thus of great benefit at temperatures below approximately 850°C, but also assists the prevention of the loss of heat energy above this temperature. As shown in Figure 5, the air or other gas or gases may be heated at 20 within a closed system containing a fan 21, the gases being continuously circulated through the refractory box 11 in which, in this example, to provide an even distribution of gas flow, there are spaced baffles 22 adjacent to the inlet and outlet of the refractory box. The tubes 23 to and from the refractory box 11 are preferably ceramic tubes designed with microwave choke to prevent radiation leaks. The baffles can also/alternatively serve to regulate the passage of gas into and out of the box.

In achieving a uniformed temperature during the initial stages of the process, greater equalisation of temperature-time profiles throughout the refractory box are obtained up to sintering temperatures, and more rapid heating is achieved. As will be described, the flow rate and gas temperature are preferably controlled.

A third technique for preventing or reducing loss of heat energy is shown in Figure 6, where a batch of ceramic articles 19 to be sintered are surrounded by a thermal screen 24, which in this embodiment, is of reticulated structure and made of ceramic material which is an absorber (or susceptor) of microwave energy and is thus heated thereby. The porous nature of the structure allows the use of the technique described in relation to Figure 5, namely the recirculation of heated air or gas,

in conjunction with the use of this thermal screen within the box 11, which as shown in Figure 6, surrounds the screen.

The relative susceptibility of the screen and batch to microwave energy may be controlled by doping the ceramic material from which the screen is made by a predetermined amount of a known, good absorber, for example silicon carbide. The reticulated nature of the screen provides low thermal mass, thereby permitting rapid temperature responses to changes in microwave power, and as stated, also allows the system to be used with circulating hot air or gas. The use of a heated screen is particularly effective at process temperatures greater than approximately 1,000°C, when heat loss by radiation becomes dominant with known methods. The screen itself could be surrounded by suitable thermal insulation.

An alternative type of thermal screen may be formed by the doping or spray coating of thermally insulating material with a known susceptor (absorber) of microwave energy. The thickness of the doped insulation or spray coating, the nature of the susceptor, and the density of the susceptor are selected to match the specific application required. Spray coatings are particularly suited to the heating of larger, individual items of variable geometry. The coating thickness and susceptance in these cases may be varied over the surface of the insulation, being greatest where the ratio of surface area to volume of the piece is large. The spray coating may be on stiff, flat board or on board shaped or profiled to match the shape or profile of the piece. A variation of this spray coated, layered screen may be more simply obtained by constructing the screen as a composite of materials of differing susceptibility, in sheet or other form. Again these alternative forms of

screen could be porous to allow the hot air or gas to be circulated through the refractory box 11.

The first and second techniques described above are optional, so that neither, one, or both can be used with the third technique, namely the provision of the thermal screen, which is used with the means and method of Figure 2.

Where the screen, wholly or partly, is conductive to electric current as well as being a susceptor to microwave energy, the material of the screen may be so formed as to provide a closed electrical circuit. The circuit may be connected to a voltage and current source 24a outside the cavity which can be independently controlled, or, preferably, controlled in conjunction with and in correct relation to the controlled microwave energy source. The provision of an independent, additional energy supply to the screen enables more precise control of temperature - time characteristics of the screen to be obtained, particularly, for example, where constraints on the choice of screen susceptor material make the required characteristics difficult to realise.

Figure 7 is a schematic, block diagram of a complete integrated control system for an embodiment of the method of the invention. Reference numerals already referred to have been used in this figure for the same parts.

As can be seen from Figure 7, the refractory box 11 has fed to it through tubes 23 the heated gas or air referred to above, this being passed through a heater 20 and fan 21. Indicated at 26 is an integrated digital control system and connected to this are lines 27, 28 respectively providing values of the temperature and flow

rate of the gas or air fed to the refractory box. Also connected to the control system 26 are lines 29 and 30 respectively which feed values of the screen temperature and the batch temperature from the refractory box. Finally a line 31 extends from the control system 26 and carries a signal to the control circuit of the magnetron to vary its power as required, although this as shown in Figure 7 goes directly to the cavity 10, since the variation in power and thus of microwave energy is transmitted into the microwave cavity. Line 31 also carries a signal to the external, independent, power supply 24a to the screen, if its conductive nature is employed. Of course not all the measurements shown in Figure 7 need be provided, since as mentioned above, the use of the heated air or gas can be omitted, and the comparable parameter for regulating the power of the magnetron could be its own measured or calculated power value, rather than the temperature of the batch or ceramic piece being heated. In particular, the heated air or gas is undesirable when firing glaze on to whiteware articles.

Using the techniques referred to above for reducing or overcoming heat loss, the control of processes associated therewith may be divided into two types:

- (a) Control of the microwave susceptance and other parameters of the thermal screen. These are predetermined and normally remain constant during the process.
- (b) Control of gas flow and/or temperature, and of power generated by the magnetron(s) with reference to set or pre-programmed temperature of or power input to the pieces. These parameters vary during the process.

The controls (a) and (b) mentioned above can be

integrated and matched to achieve the required material properties/microstructure of the piece or pieces. Optimum control of the total scheme is achieved by control of the variable parameters within (b) by a multi-input, adaptive/self-tuning digital control scheme. Control of gas flow and its heating external to the cavity enables a relative temperature-time characteristics of the thermal screen and batch to be controlled. The control scheme may include or be assisted by input data on the loss factor of ceramic materials at elevated temperatures.

As described, except when firing glaze on to whiteware articles, or with products where a still atmosphere is desired, the use of circulating hot air/gas is normally of great benefit at process temperatures lower than approximately 850°C, and in an embodiment using all three techniques, the stacking arrangement shown in Figure 4 would be used in conjunction with the use of the thermal screen and the circulation of the heated air/gas. At temperatures above approximately 1,000°C, the stacking system of Figure 4 could be used with the thermal screen of Figure 6 without the use of the heated gas/air.

The combination of thermal screen and hot gas forms a hybrid system of heating controlled by an integrated controller which compares measured values with set or computed values from a mathematical model of the system. The heating of the thermal screen can be by virtue of the microwave energy alone or with the electrical heating.

The method described is preferably continuously controlled and the integrated control of all the variables prevents thermal runaway and enables uniform heating to be achieved within the ceramic piece and

throughout the refractory box. The method can thus enhance the uniformity, consistency and speed of the microwave heating and firing of the piece.

CLAIMS

1. A method of heating ceramic material in an interior of an enclosure, comprising providing a variable power source of microwave energy, providing in said interior of the enclosure a thermal screen which is around the ceramic material, in use, and which is heated by said microwave energy, operating said source to supply microwave energy to said interior of said enclosure containing said ceramic material, in use, and continuously controlling the power of said source in response to a difference between a set value of a parameter of the system, and a measured or calculated value of the parameter during operation of the method.
2. A method as claimed in Claim 1, comprising passing heated gas through the enclosure, the gas passing around the ceramic material therein, in use.
3. A method as claimed in Claim 2, comprising heating said gas externally of said enclosure and circulating the heated gas in a closed system including a fan.
4. A method as claimed in Claim 2 or Claim 3, comprising passing the heated gas through the thermal screen.
5. A method as claimed in any one of the preceding claims, comprising electrically heating the thermal screen.
6. A method as claimed in any one of Claims 2 to 4, comprising electrically heating the thermal screen and controlling the heating of the ceramic material by an integrated control of gas temperature and flow, and thermal screen temperature, based on a comparison of

their measured values with set or computed values from a mathematical model of the system.

7. Apparatus for heating ceramic material comprising an enclosure having an interior in which said ceramic material is intended to be received, a thermal screen in said interior around said ceramic material, in use, a variable power source of microwave energy outside the enclosure operable to supply microwave energy to said interior of the enclosure containing said ceramic material, in use, and means for continuously controlling the power of said source, in use, in response to a difference between a set value of a parameter of the system, and a measured or calculated value of the parameter during the heating.

8. Apparatus as claimed in Claim 7, comprising means for stacking ceramic material items to be heated, in use, one above the other with respective spaces between adjacent items above and/or below.

9. Apparatus as claimed in Claim 7 or Claim 8, wherein means are provided for passing heated gas, in use, through said enclosure and around said ceramic material to be heated.

10. Apparatus as claimed in Claim 9, wherein means are provided for heating said gas externally of said enclosure, and fan means are provided for circulating the heated gas in a closed system.

11. Apparatus as claimed in any one of Claims 8 to 10, comprising respective baffles adjacent an inlet and an outlet of a refractory box in which the ceramic material to be heated is disposed.

12. Apparatus as claimed in Claim 9 or Claim 10,

wherein said heated gas flows, in use, to said enclosure in ceramic conduits.

13. Apparatus as claimed in Claim 9 or Claim 10, wherein the heated gas is arranged to flow through the thermal screen.

14. Apparatus as claimed in any one of Claims 7 to 13, wherein the thermal screen is of reticulated structure.

15. Apparatus as claimed in any one of Claims 7 to 14, wherein the thermal screen is of ceramic material.

16. Apparatus as claimed in any of Claims 7 to 15, wherein the susceptibility of the thermal screen to microwave energy is controlled by doping the screen material with a predetermined amount of susceptor.

17. Apparatus as claimed in any one of Claims 7 to 16, wherein the thermal screen is surrounded by thermal insulation.

18. Apparatus as claimed in any one of Claims 7 to 13, wherein the thermal screen is of thermally insulating material doped with a susceptor of microwave energy.

19. Apparatus as claimed in any one of Claims 7 to 13, wherein the thermal screen is of thermally insulating material spray coated with a susceptor of microwave energy.

20. Apparatus as claimed in Claim 19, wherein coating thickness and/or susceptance is varied over the surface of the thermally insulating material.

21. Apparatus as claimed in Claim 19 or Claim 20, wherein the coating is on material shaped/profiled to

match the shape/profile of ceramic material, in use, to be heated.

22. Apparatus as claimed in any one of Claims 18 to 21, wherein the thermal screen is porous.

23. Apparatus as claimed in any one of Claims 7 to 13, wherein the thermal screen is composed as a composite structure of materials of differing susceptance.

24. Apparatus as claimed in any one of Claims 7 to 23, comprising means for electrically heating the thermal screen.

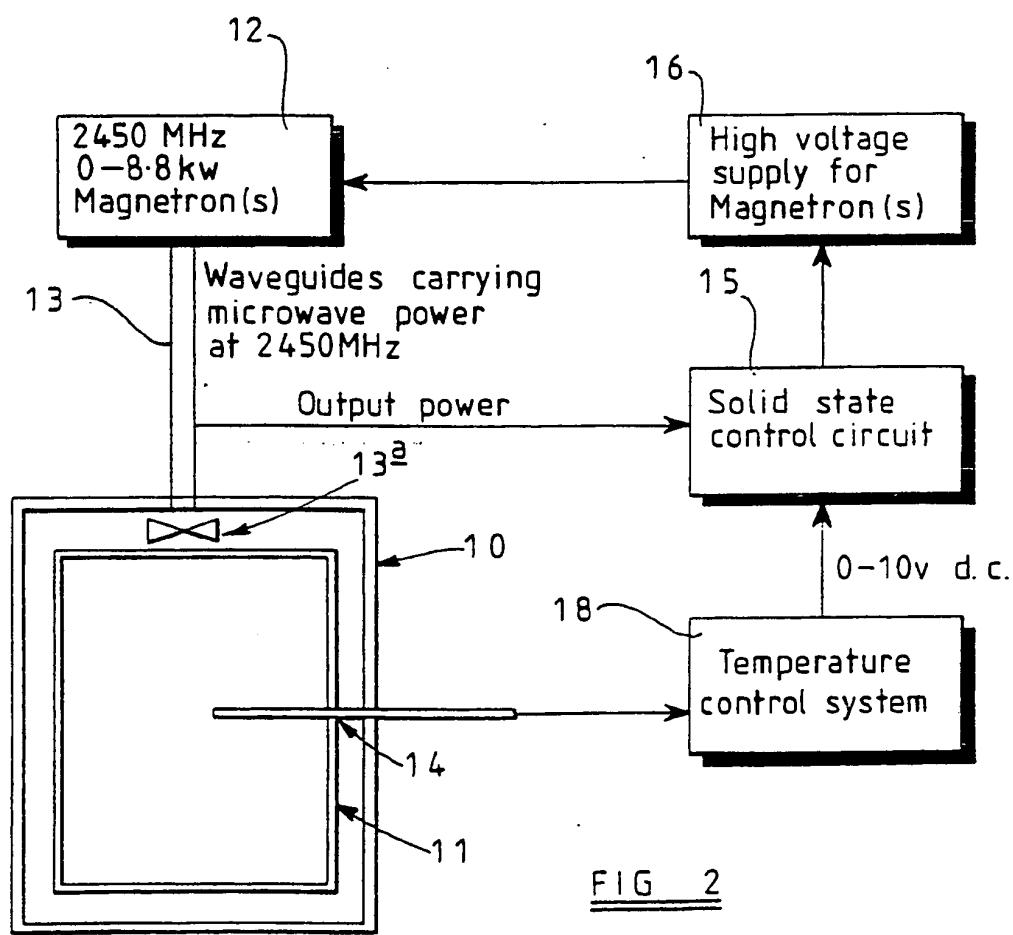
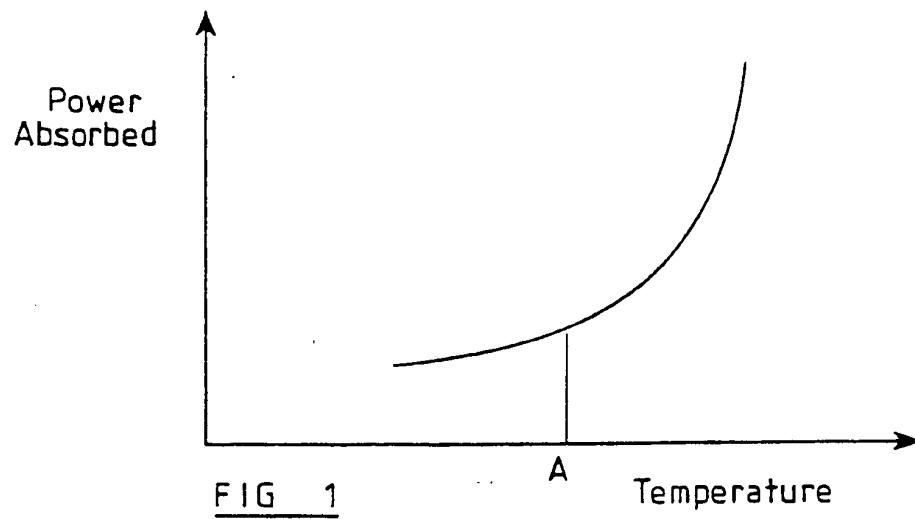
25. Apparatus as claimed in Claim 24, comprising a closed electrical circuit to and from the thermal screen, the circuit including a voltage source.

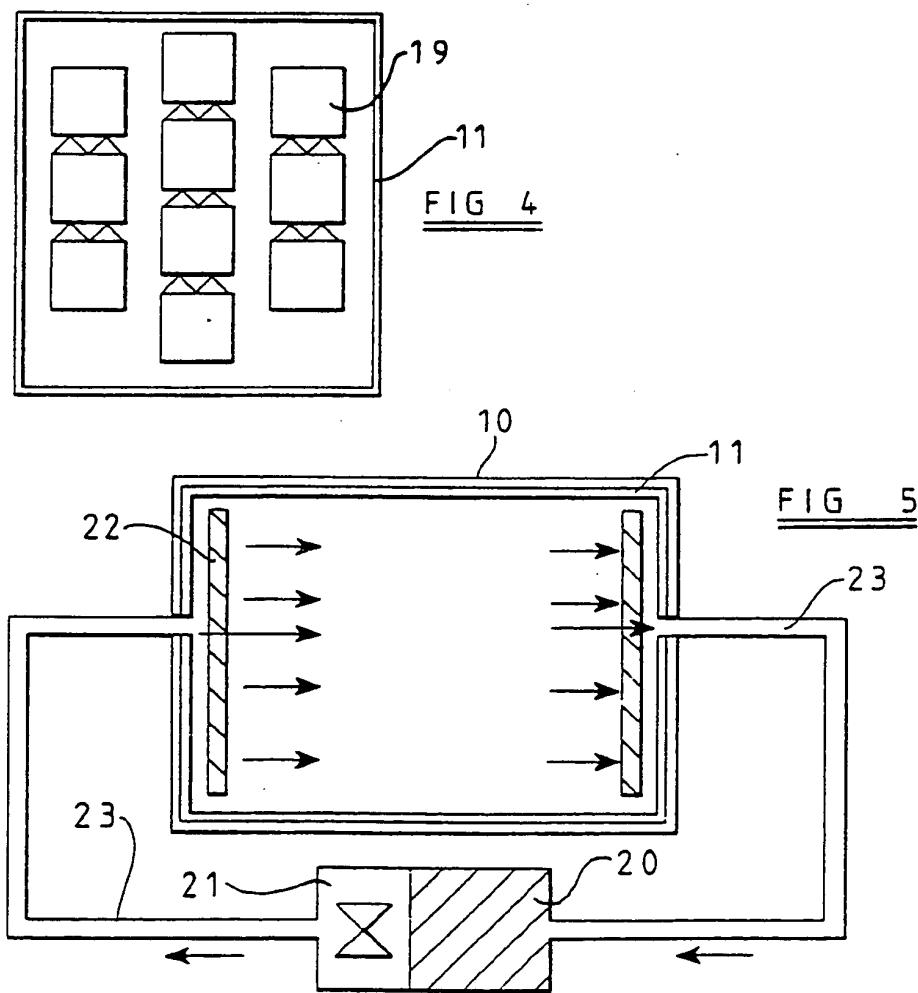
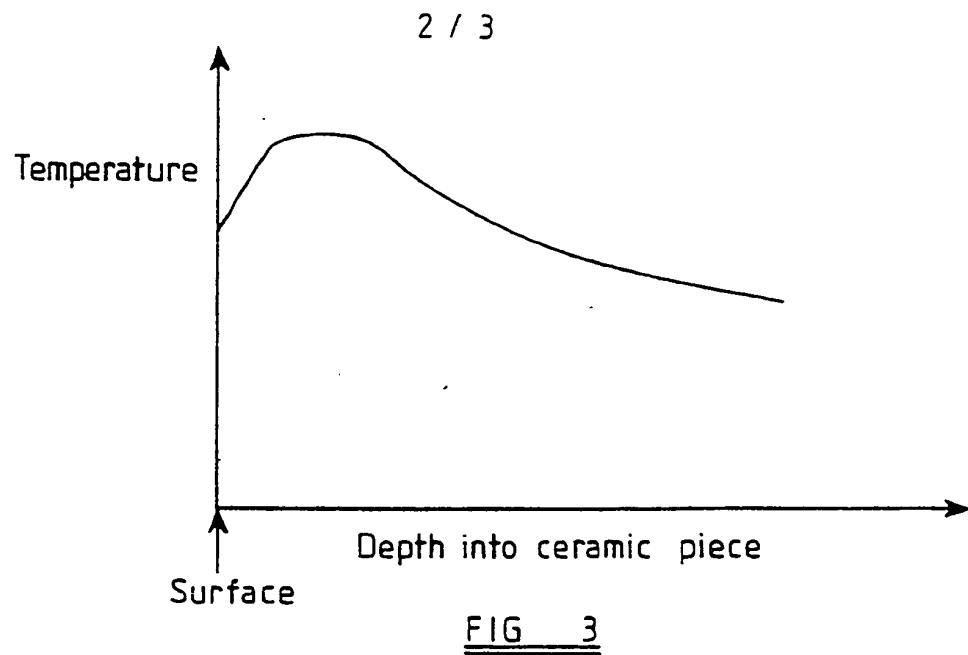
26. Apparatus as claimed in Claim 25, comprising means for controlling said voltage source in conjunction with said control of the source of microwave energy.

27. Apparatus as claimed in Claim 26, wherein said controls of the voltage source and microwave energy source respectively are incorporated in an integrated control which continuously receives said measured or calculated values of the parameters and compares them to said set value.

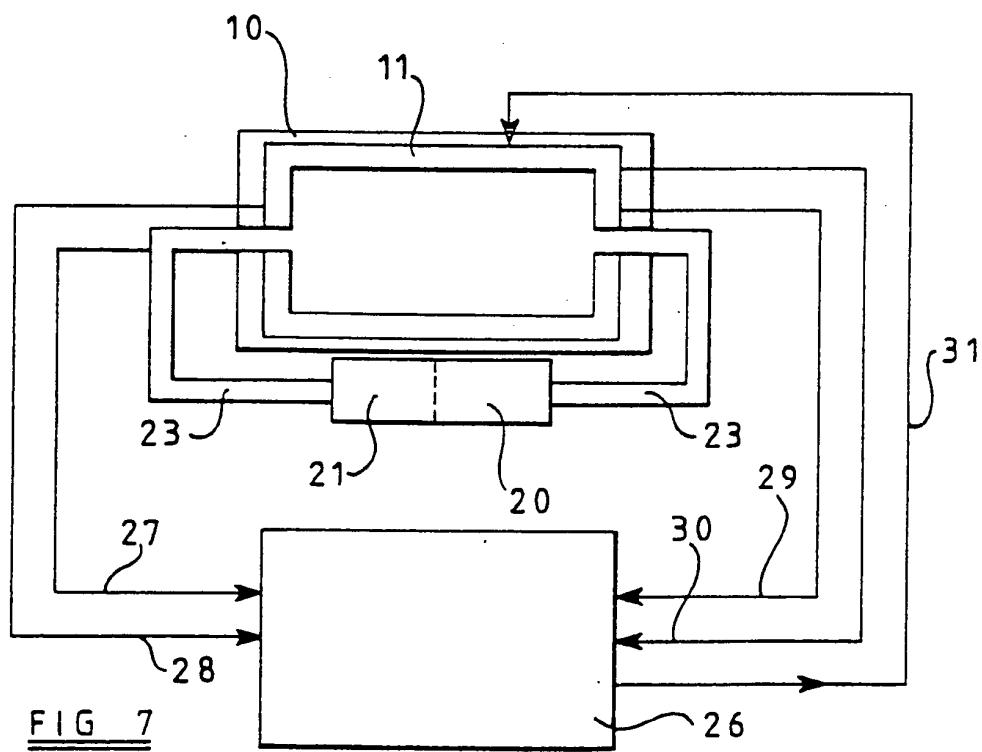
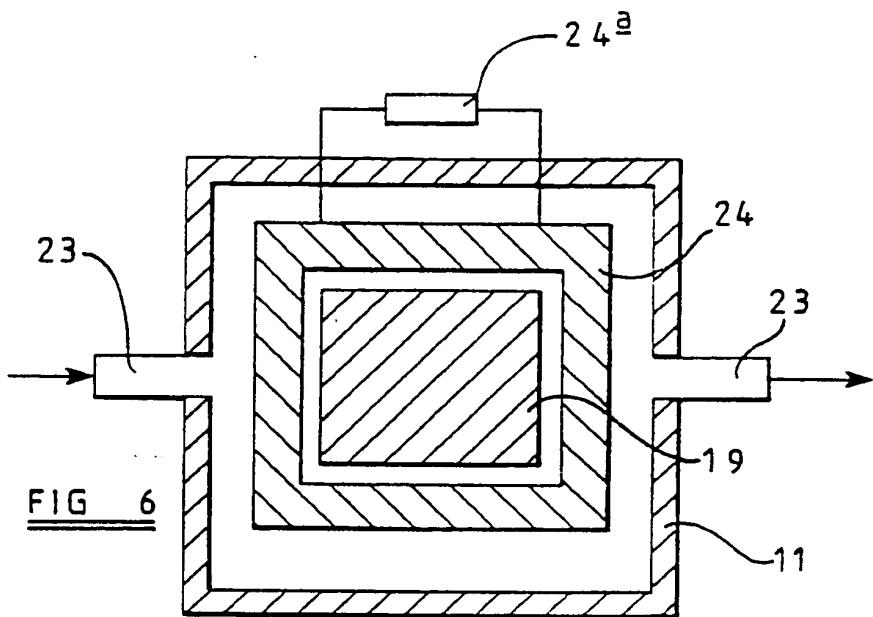
28. Apparatus as claimed in Claim 24 when appended to Claim 9, comprising an integrated control of gas temperature and flow, and thermal screen temperature, based on a comparison of their measured values with set or computed values from a mathematical model of the system.

1 / 3





3 / 3



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 92/02277

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>9</sup>		
<p>According to International Patent Classification (IPC) or to both National Classification and IPC</p> <p>Int.Cl. 5 H05B6/80</p>		
II. FIELDS SEARCHED		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	H05B	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No <sup>13</sup>
Y	US,A,4 307 277 (S. MAEDA ET AL.) 22 December 1981 see column 2, line 30 - column 3, line 13; figures 3-5 --- GB,A,2 227 397 (CEM CORP.) 25 July 1990 see page 7, line 17 - page 13, line 14; figures 1-6 --- EP,A,0 412 019 (REGIE NATIONALE DES USINES RENAULT) 6 February 1991 see column 1, line 1 - column 2, line 50; figure 1 --- -/--	1,7, 15-18
A		4,9, 13-15,22
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
19 MARCH 1993	30.03.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	ALBERTSSON E.G.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 15, no. 229 (E-1076) 11 June 1991 & JP,A,30 67 489 ( YUZURU MATSUBARA ) 22 March 1991 see abstract ---	19-21
A	US,A,4 822 966 (Y. MATSUBARA) 18 April 1989 ---	
A	US,A,4 880 578 (C.E. HOLCOMBE ET AL.) 14 November 1989 -----	

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

GB 9202277  
SA 67515

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 19/03/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4307277	22-12-81	JP-C- 1296667 JP-A- 55023826 JP-B- 60017990 JP-C- 1372978 JP-A- 55049688 JP-B- 61038393	20-01-86 20-02-80 08-05-85 07-04-87 10-04-80 29-08-86
GB-A-2227397	25-07-90	US-A- 5066843 AU-A- 1285692 AU-B- 627819 AU-A- 4789690 CH-A- 680239 DE-A- 4000515 FR-A- 2641855 FR-A- 2648219	19-11-91 14-05-92 03-09-92 26-07-90 15-07-92 26-07-90 20-07-90 14-12-90
EP-A-0412019	06-02-91	FR-A- 2650627	08-02-91
US-A-4822966	18-04-89	None	
US-A-4880578	14-11-89	None	